

# Meta-Plaquette Expansion for the Triplet Excitation Spectrum in $\text{CaV}_4\text{O}_9$

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## Abstract

We study antiferromagnetic,  $S = 1/2$  Heisenberg models with nearest and second neighbor interactions on the one-fifth depleted square lattice which describes the spin degrees of freedom in the spin-gap system  $\text{CaV}_4\text{O}_9$ . The meta-plaquette expansion for the triplet excitation spectrum is extended to fifth order, and the results are compared with experimental data on  $\text{CaV}_4\text{O}_9$ . We attempt to locate the phase boundary between magnetically ordered and gapped phases.

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The physics of low-dimensional Heisenberg antiferromagnets has been a subject of much interest. These models represent a class of quantum many-body Hamiltonians which accurately model real materials and whose properties can be calculated by a number of controlled analytical and numerical methods.

Recently, the observation of spin gaps in the quasi-2D material  $\text{CaV}_4\text{O}_9$  [1–4] has attracted much attention from theorists. In this layered material,  $S = 1/2$  vanadium atoms form a one-fifth depleted square lattice which we will refer to as the CAVO lattice, and which is shown in Fig. 1. It is expected that low energy properties of  $\text{CaV}_4\text{O}_9$  are described by the antiferromagnetic Heisenberg model with four kinds of exchange interactions:  $J_1$  and  $J'_1$  for the nearest-neighbor intra- and inter-plaquette coupling respectively, and  $J_2$  and  $J'_2$  for the second-neighbor interaction, as shown in Fig. 1. One is thus led to consider the following Hamiltonian:

$$H = J_1 \sum_{(i,j)} \mathbf{S}_i \cdot \mathbf{S}_j + J'_1 \sum_{(i,k)} \mathbf{S}_i \cdot \mathbf{S}_k + J_2 \sum_{(i,l)} \mathbf{S}_i \cdot \mathbf{S}_l + J'_2 \sum_{(i,m)} \mathbf{S}_i \cdot \mathbf{S}_m, \quad (1)$$

where the sums run over nearest-neighbor bonds within plaquettes ( $J_1$ ), nearest-neighbor bonds between plaquettes ( $J'_1$ ), second-neighbor bonds within plaquettes ( $J_2$ ), and second-neighbor bonds between plaquettes ( $J'_2$ ). This Hamiltonian has the property that every spin is equivalent, just as every vanadium atom in  $\text{CaV}_4\text{O}_9$  is equivalent.

To understand the mechanism of the gap formation, a variety of methods, including quantum Monte Carlo simulation [5,6], perturbative and high-temperature series expansion [4,7–11], exact diagonalization [10,12], DMRG method [13], spin-wave theory [14], and other techniques [15–17] have been applied to this model. Based on simple considerations, most authors have assumed  $J_1 \simeq J'_1$ ,  $J_2 \simeq J'_2$ , and  $J_1 > J_2$ , and with this assumption, the experimental data is best supported by assuming that the second-neighbor interactions are roughly half the first-neighbor interactions: but the fits are not entirely satisfactory.

Recently, Pickett [18] has used LDA calculations to study the magnetic properties of  $\text{CaV}_4\text{O}_9$ . He argues that out-of-plane distortions in the arrangement of the vanadium atoms are quite important. The one-fifth depleted square lattice of vanadium atoms is actually made up of two (planar) layers, slightly above and below one  $ab$ -plane, and each forming a square lattice of “meta-plaquettes.” These meta-plaquettes are to be distinguished from the plaquettes considered before by Ueda *et al.* [19] and other authors in the “plaquette RVB” (PRVB) scenario. The plaquettes involve nearest-neighbor spins, two of them lying in the upper layer and two in the lower layer. In this case, a significant second-neighbor interaction is expected within the plaquettes. In contrast, the meta-plaquettes of Pickett lie either entirely in the upper or entirely in the lower layer. Pickett argues that although the spins within a meta-plaquette are further apart than spins between two neighboring meta-plaquettes, various quantum-chemical arguments conspire to make the interactions within meta-plaquettes the strongest. He finds that to leading approximation the magnetic system should be regarded as decoupled meta-plaquettes. One important point to note is that within a meta-plaquette the interactions are expected to be primarily between neighboring spins only.

On the experimental side, a neutron inelastic scattering experiment has been recently carried out by Kodama *et al* [4], and the triplet excitation spectrum was obtained. They

also reported that the theoretical results using the second order perturbation from the disconnected meta-plaquette model, which is defined by  $J_1 = J'_1 = J_2 = 0$ , agrees with the experimental results when  $J'_2 = 14.73$ ,  $J_1 = J'_1 = 5.76$ , and  $J_2 = 1.25(\text{meV})$ . (In their fitting procedure,  $J_1 = J'_1$  is assumed.). However, there are some mistakes in their calculation. These mistakes have been corrected by Fukumoto and Oguchi [11], and they also extend the results to third order for given values of  $J'_1/J_1$  and  $J_2/J_1$ . In the third order perturbation expansion, the exchange parameters for  $\text{CaV}_4\text{O}_9$  are determined as  $J'_2 = 14.0(1)$ ,  $J_1 = J'_1 = 6.8(2)$ , and  $J_2 = 1.7(2)(\text{meV})$ . Using these exchange parameters and the technique of numerical diagonalization of finite lattices, Takano and Sano [20] calculated the magnetic susceptibility  $\chi$ , and found the experimental data to be about 30% smaller than the theoretical results. They interpret this as due to the 30% volume fraction of nonmagnetic components in the  $\text{CaV}_4\text{O}_9$  sample, and this explanation is also consistent with other experimental data. In this report, we extend the meta-plaquette series expansions for the triplet excitation spectrum to fifth order.

To carry out the expansion about disconnected meta-plaquettes, we rewrite the Hamiltonian in Eq. (1) as:

$$H/J'_2 = H_0 + xV \quad (2)$$

where  $H_0$  and  $V$  are the unperturbed Hamiltonian and perturbation, respectively, and  $x$  is the expansion parameter. They are defined as:

$$\begin{aligned} H_0 &= \sum_{(i,m)} \mathbf{S}_i \cdot \mathbf{S}_m \\ V &= \sum_{(i,j)} \mathbf{S}_i \cdot \mathbf{S}_j + y_1 \sum_{(i,k)} \mathbf{S}_i \cdot \mathbf{S}_k + y_2 \sum_{(i,l)} \mathbf{S}_i \cdot \mathbf{S}_l \\ x &= J_1/J'_2 \\ y_1 &= J'_1/J_1 \\ y_2 &= J_2/J_1 \end{aligned} \quad (3)$$

We use the linked-cluster expansion method which has been previously reviewed in several articles [21–23]. Here we have performed a three parameter ( $x$ ,  $y_1$  and  $y_2$ ) meta-plaquette series expansion for the triplet elementary excitation spectrum up to fifth order. The excitation spectrum takes the form:

$$\Delta(k_x, k_y)/J'_2 = \sum_{i=0}^5 \sum_{j,k,m,n} a_{i,j,k,m,n} x^i y_1^j y_2^k [\cos(mk_x + nk_y) + \cos(nk_x - mk_y)]/2 \quad (4)$$

Where  $a_{i,j,k,m,n}$  are the expansion coefficients. Up to order  $i = 5$ , there are a total of 698 non-zero terms in the series for general  $(k_x, k_y)$ : since this requires an inordinate amount of space to reproduce in print, it is available from the authors on request. Instead, in Table I, we list the series for fixed  $(k_x, k_y) = (0, 0)$  and  $(\pi, \pi)$ . Our results agree with the results of Fukumoto and Oguchi [11] and extend the series by two orders. We also agree with the results of Gelfand and Singh [8] who only considered the  $(0, 0)$  gap in the case  $J_1 = J'_1$  and  $J_2 = 0$ .

We first seek to refine the values of the exchange parameters for  $\text{CaV}_4\text{O}_9$  using our extended series. Fig. 2 shows the dispersion curve, based on the parameter values  $J'_2 = 14.0$ ,

$J_1 = J'_1 = 6.8$  and  $J_2 = 1.7(\text{meV})$  of Fukumoto and Oguchi [11], evaluated by direct summation of the expansion to 2nd, 3rd, 4th and 5th order. The experimental points of Kodama *et al.* [4] are also shown. It is clear from the figure that the higher terms are small, for this region of parameters, and the curves are almost indistinguishable, except near the point  $(\pi, \pi)$ . Further experimental data at this point would allow a refinement of the parameters, but without this there is little basis for doing so.

Within the  $(x, y_1, y_2)$  parameter space there will be a critical surface separating a phase with long range antiferromagnetic order (at  $T = 0$ ) from a gapped spin-liquid phase (in which the real material  $\text{CaV}_4\text{O}_9$  lies). Although a 6-term series is really too short to determine critical points with any accuracy, we are able to make a first estimate of this, at least in the region where the minimum gap occurs at  $(0, 0)$ . To do this we fix values of  $y_1$  and  $y_2$  and analyze Dlog Padé approximants [24] to the series for  $\Delta(x)$  which vanishes at  $x_c$ . Figure 3 shows slices of the critical surface in the  $(x, y_2)$  plane for various choices of  $y_1$ . The lines separate an upper gapless antiferromagnetic phase from the lower gapped phase. The real material has  $x = 0.49$ ,  $y_1 = 1$ ,  $y_2 = 0.25$  and lies well within the gapped phase. The vanishing of the gap is characterized by an exponent  $\nu$ , which we estimate as  $\simeq 0.7$ . This suggests that the transition may lie in the universality class of the classical  $d = 3$  Heisenberg model.

Finally we investigate the qualitative form of the dispersion curve for a range of parameter values within the gapped phase. Fig. 4 shows this for fixed  $x = 0.4$ ,  $y_1 = 1$  and various  $y_2$ . For small  $y_2$  the shape of the dispersion curve is broadly similar to the experimental one, with a minimum at  $(0, 0)$  and a maximum at  $(\pi, \pi)$ . For  $y_2 \simeq 0.5$  the dispersion along the  $k_x$  and  $k_y$  directions becomes quite flat and for  $y_2 > 0.5$  the minimum shifts from  $(0, 0)$  to  $(\pi, 0)$ . It is interesting to speculate on whether these regions could be achievable in  $\text{CaV}_4\text{O}_9$  by suitable modification of the structure or by external strains.

In conclusion we have extended the meta-plaquette expansion for the triplet excitation spectrum of the Heisenberg model on the CAVO lattice by two terms, to 5th order. We are able to locate at least part of the critical surface separating gapless and gapped phases. The shape of the dispersion curve shows interesting variation with  $J_2$ , the intra-plaquette second-neighbor exchange parameter, for fixed values of the other parameters. In the region of parameter space for the real material  $\text{CaV}_4\text{O}_9$  the contribution of the higher terms is quite small and we are unable to further refine the values of proposed by Fukumoto and Oguchi. Further experimental data particularly around the  $(\pi, \pi)$  point would allow this to be done.

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## FIGURES

FIG. 1. The CAVO lattice, with sites indicated by circles. The full and open circles represent vanadium ions slightly above and below the plane, respectively. The couplings  $J_1$ ,  $J'_1$ ,  $J_2$ , and  $J'_2$  are indicated by thick solid, thin solid, thin dashed, and thick dashed lines, respectively. Note that the meta-plaquette centers lie on a square lattice with spacing  $b$  which is  $\sqrt{5}$  times the distance between nearest-neighbor sites. In characterizing the excitation spectrum we take  $b = 1$  and rotate the coordinate system so that the lines between nearest-neighbor meta-plaquette centers define the  $x$  and  $y$  axes.

FIG. 2. Triplet excitation spectra along high-symmetry directions as estimated by direct sum of meta-plaquette expansions to order  $x^2$  (dotted line),  $x^3$  (short dashed line),  $x^4$  (long dashed line), and  $x^5$  (solid line), for  $J_1 = J'_1 = 6.8$ ,  $J_2 = 1.7$  and  $J'_2 = 14.0$ (meV). Also shown as full points are the experimental data by Kodama *et al.* [4]

FIG. 3. Partial phase boundary for  $y_1 = 0, 0.5, 1$  of the CAVO lattice Heisenberg model, as determined from meta-plaquette expansions. The points with error bars and a solid line to guide the eye indicate the phase boundary where the  $(0,0)$  gap vanishes. The cross shows the position of  $\text{CaV}_4\text{O}_9$  in the parameter space.

FIG. 4. Triplet excitation spectra along high-symmetry directions as estimated by Padé approximants to the series to order  $x^5$ , for  $y_2 = 0, 0.25, 0.5$ , and  $1$  (as shown) at  $x = 0.4$ ,  $y_1 = 1$ .

# TABLES

TABLE I. Series coefficients for the meta-plaquette expansion of the triplet excitation spectrum  $\Delta(k_x, k_y)/J'_2 = \sum_{i,j,k} a_{i,j,k}(k_x, k_y) x^i y_1^j y_2^k$ . Nonzero coefficients  $a_{i,j,k}$  for  $(k_x, k_y) = (0, 0)$  and  $(\pi, \pi)$  up to order  $i = 5$  are listed.

$(i, j, k)$	$a_{i,j,k}(0, 0)$	$a_{i,j,k}(\pi, \pi)$	$(i, j, k)$	$a_{i,j,k}(0, 0)$	$a_{i,j,k}(\pi, \pi)$
(0, 0, 0)	1.000000000	1.000000000	(4, 1, 3)	$-1.274215356 \times 10^{-1}$	$1.274215356 \times 10^{-1}$
(1, 0, 0)	-1.333333333	1.333333333	(4, 2, 0)	$1.074058127 \times 10^{-1}$	$-7.455165932 \times 10^{-2}$
(1, 0, 1)	$6.666666667 \times 10^{-1}$	$6.666666667 \times 10^{-1}$	(4, 2, 1)	$2.690073898 \times 10^{-1}$	-1.082138472
(1, 1, 0)	$6.666666667 \times 10^{-1}$	$-6.666666667 \times 10^{-1}$	(4, 2, 2)	$3.365078472 \times 10^{-2}$	$-6.298532394 \times 10^{-1}$
(2, 0, 0)	$-4.050925926 \times 10^{-1}$	$3.935185185 \times 10^{-2}$	(4, 3, 0)	$-8.134986977 \times 10^{-2}$	$-6.022038137 \times 10^{-3}$
(2, 0, 1)	$8.888888889 \times 10^{-1}$	$-8.888888889 \times 10^{-1}$	(4, 3, 1)	$-7.119885055 \times 10^{-2}$	$2.658296322 \times 10^{-1}$
(2, 0, 2)	$6.597222222 \times 10^{-2}$	$6.597222222 \times 10^{-2}$	(4, 4, 0)	$1.385933255 \times 10^{-2}$	$3.384182408 \times 10^{-2}$
(2, 1, 0)	$8.564814815 \times 10^{-2}$	$8.564814815 \times 10^{-2}$	(5, 0, 0)	$-2.353587765 \times 10^{-1}$	$9.367446624 \times 10^{-2}$
(2, 1, 1)	$-4.444444444 \times 10^{-1}$	$4.444444444 \times 10^{-1}$	(5, 0, 1)	$4.839207165 \times 10^{-1}$	$2.629675619 \times 10^{-1}$
(2, 2, 0)	$6.597222222 \times 10^{-2}$	$-3.229166667 \times 10^{-1}$	(5, 0, 2)	$-9.949929589 \times 10^{-1}$	$7.710126890 \times 10^{-1}$
(3, 0, 0)	$-2.817804784 \times 10^{-1}$	$1.440972222 \times 10^{-1}$	(5, 0, 3)	$9.187244689 \times 10^{-2}$	$-3.584889115 \times 10^{-2}$
(3, 0, 1)	$8.875064300 \times 10^{-2}$	$-3.012956533 \times 10^{-1}$	(5, 0, 4)	$-8.793820229 \times 10^{-2}$	$8.793820229 \times 10^{-2}$
(3, 0, 2)	$-3.766718107 \times 10^{-1}$	$3.766718107 \times 10^{-1}$	(5, 0, 5)	$1.620527344 \times 10^{-2}$	$1.620527344 \times 10^{-2}$
(3, 0, 3)	$7.607542438 \times 10^{-3}$	$7.607542438 \times 10^{-3}$	(5, 1, 0)	$4.041080312 \times 10^{-1}$	$-4.210403484 \times 10^{-1}$
(3, 1, 0)	$3.118730710 \times 10^{-1}$	$-2.667582948 \times 10^{-1}$	(5, 1, 1)	$-4.870132049 \times 10^{-1}$	$-4.980867393 \times 10^{-1}$
(3, 1, 1)	$5.377121914 \times 10^{-2}$	$1.100983796 \times 10^{-1}$	(5, 1, 2)	1.203414600	-1.113097779
(3, 1, 2)	$1.883359053 \times 10^{-1}$	$-1.883359053 \times 10^{-1}$	(5, 1, 3)	$-5.450494770 \times 10^{-2}$	$-6.017493539 \times 10^{-2}$
(3, 2, 0)	$-8.644788452 \times 10^{-2}$	$-8.135207690 \times 10^{-2}$	(5, 1, 4)	$4.396910114 \times 10^{-2}$	$-4.396910114 \times 10^{-2}$
(3, 2, 1)	$-1.073173868 \times 10^{-1}$	$-3.426568930 \times 10^{-1}$	(5, 2, 0)	$-3.524127097 \times 10^{-1}$	$6.926810815 \times 10^{-1}$
(3, 3, 0)	$7.607542438 \times 10^{-3}$	$-8.186246142 \times 10^{-3}$	(5, 2, 1)	$1.178079295 \times 10^{-1}$	$-4.130088800 \times 10^{-1}$
(4, 0, 0)	$-2.039154182 \times 10^{-1}$	$-2.576864986 \times 10^{-2}$	(5, 2, 2)	$-5.404083450 \times 10^{-1}$	-1.147271044
(4, 0, 1)	$6.358148317 \times 10^{-1}$	$-3.967625126 \times 10^{-1}$	(5, 2, 3)	$1.206115343 \times 10^{-3}$	-1.006669452
(4, 0, 2)	$-1.728981197 \times 10^{-1}$	$1.055808005 \times 10^{-1}$	(5, 3, 0)	$2.350225176 \times 10^{-1}$	$-5.747589936 \times 10^{-1}$
(4, 0, 3)	$2.548430713 \times 10^{-1}$	$-2.548430713 \times 10^{-1}$	(5, 3, 1)	$5.681996667 \times 10^{-2}$	$-2.997134488 \times 10^{-2}$
(4, 0, 4)	$1.385933255 \times 10^{-2}$	$1.385933255 \times 10^{-2}$	(5, 3, 2)	$1.056067425 \times 10^{-1}$	$3.714433690 \times 10^{-1}$
(4, 1, 0)	$9.481864669 \times 10^{-2}$	$-3.738896059 \times 10^{-2}$	(5, 4, 0)	$-9.802141001 \times 10^{-2}$	$2.993556466 \times 10^{-1}$
(4, 1, 1)	$-6.426060778 \times 10^{-1}$	$5.469359068 \times 10^{-1}$	(5, 4, 1)	$-3.779095786 \times 10^{-2}$	$2.653503873 \times 10^{-1}$
(4, 1, 2)	$5.705034556 \times 10^{-2}$	$2.893338312 \times 10^{-2}$	(5, 5, 0)	$1.620527344 \times 10^{-2}$	$-4.403051591 \times 10^{-2}$









